OUR ASTRONOMICAL COLUMN.

ASTRONOMICAL OCCURRENCES IN FEBRUARY.

Feb. 1. 19h. 10m. to 20h. 29m. Moon occults β^2 Scorpii (mag. 5·2).
  1. 19h. 10m. to 20h. 28m. Moon occults β^1 Scorpii (mag. 3·0).
  3. 0h. Mercury at greatest elongation (18° 17′ E.).
  6. 17h. Jupiter in conjunction with moon. Jupiter 5° 26′ S.
  8. 17h. Venus in conjunction with moon. Venus 3° 9′ N.
  9. 9h. Mercury in conjunction with moon. Mercury 2° 23′ S.
  12. 7h. 40m. to 8h. 18m. Moon occults ε Piscium (mag. 4·5).
  14. 5h. 53m. to 6h. 45m. Moon occults σ Arietis (mag. 5·5).
  14. 11h. Venus in inferior conjunction with the sun.
  16. 6h. 24m. to 7h. 18m. Moon occults i Tauri (mag. 5·1).
  17. 11h. 41m. Minimum of Algol (β Persei).
  20. 8h. 30m. Minimum of Algol (β Persei).

VARIABILITY OF THE SATELLITES OF SATURN.—In the *Bulletin de la Société Astronomique de France* (January 1902), M. L. Rudaux directs attention to the probable variation in the brightness of the satellites Titan and Japetus, from evidence furnished by observations since 1892. He concludes that in the case of Titan the change is about half a magnitude, from 8·0 to 8·5, and, moreover, the variation appears to occur regularly at the same parts of the satellite's orbit. Maxima occur near and just after west elongation, and minima when the satellite is between superior conjunction and east elongation. A suggested explanation supposes the existence of fixed regions of different brightness and the rotation period equal to the time of revolution, as in the case of our own moon. There is a rapid passage from maximum to minimum.

The satellite Japetus is also thought to have equal periods for rotation and revolution, and the observation of Cassini is confirmed that the body almost becomes invisible in the eastern portion of its orbit. The variation is from the ninth to twelfth magnitude.

Prof. T. J. J. See refers to the variable visibility of Japetus in an article giving measures of the diameters of the satellites of Jupiter and Saturn in *Astronomische Nachrichten* (Bd. 157, No. 3764). He says, "The disc of Titan is rather obscure, but that of Japetus is even more so; in fact, only one side gives sufficient light to enable the observer to recognise a disc. This is visible when the satellite precedes the planet."

MAGNETIC OBSERVATIONS DURING TOTAL SOLAR ECLIPSE, MAY 18, 1901.—In a pamphlet reprinted from the *Overgedrukt uit het Natuurkundig Tijdschrift voor Ned-Indië* (vol. lxi., part iii. pp. 173–193), Dr. W. van Bemmelen presents the observations undertaken at Batavia and Karang Sago (Sumatra) during the last total eclipse of the sun on May 18, 1901. The determinations were made on behalf of the Batavia Observatory in response to the appeal of Dr. L. A. Bauer for accurate measures. The observations were made both visually and by means of self-recording photographic apparatus, reproductions from these latter being given. Although complicated by the presence of various common disturbances, the curves show decided irregularities about the time of eclipse which are thought to be due to the occurrence of that phenomenon. The observations at Batavia were only rendered possible by the courtesy of the Electric Car Company in stopping traffic over their lines from 11.30 a.m. to 2.30 p.m. on the day of eclipse.

SIMULTANEOUS VISIBILITY OF SUN AND TOTAL LUNAR ECLIPSE.—In the *Transactions* of the Vienna Academy of Sciences (Section of Mathematics and Natural Sciences) No. xxiv. pp. 263–271, Herr Dr. C. Hillebrand directs attention to the possible observation of both sun and total lunar eclipse at such times when the phenomenon occurs as the moon is rising or setting. As the refraction at the horizon is greater than the diameter of the lunar or solar disc, the sun will be visible after true sunset or before true sunrise; and the conditions for the eclipsed moon to be thus seen may be fulfilled at certain localities during the lunar eclipses of April 22 and October 16 of the present year.

THE VALIDITY OF THE IONISATION THEORY.[1]

Introduction.—The theory of electrolytic dissociation as advanced by Arrhenius in 1887 is based primarily upon the facts that the molecular conductivity of solutions increases with the dilution, that substances which, when dissolved, conduct electricity also have abnormally low molecular weights in such solutions when tested by osmotic or freezing- or boiling-point methods, and that the so-called degree of dissociation may be calculated from the electrical conductivity or the results of the molecular weight determinations. In his original article, Arrhenius states that the phenomena of electrolysis, when viewed from the standpoint of thermodynamics, require the assumption of free ions, as was pointed out by Clausius, and that the well-known additive properties of solutions support this hypothesis. Arrhenius sought to save van 't Hoff's theory of solutions from having but a limited application, and to extend it.

Van 't Hoff found it necessary to introduce the factor i in the case of electrolytic aqueous solutions in order to make them conform to the gas equation. This factor Arrhenius calculated from the electrical conductivity on the one hand and from molecular weight determinations on the other, the resulting figures showing an agreement to within 5 to 15 per cent. The agreement was not good, and the results were obtained exclusively from aqueous solutions. The non-aqueous solutions then known were practically non-conductors, and appeared to be fairly normal as regards van 't Hoff's theory, so that non-aqueous solutions in general came to be regarded as having normal molecular weights and as being non-conductors.

Behaviour of Non-aqueous Electrolytic Solutions.—Previous work has already shown that non-aqueous electrolytic solutions are frequently abnormal in the light of the ionisation theory. Thus in many cases the molecular conductivity decreases with increased dilution, *e.g.* NaI and NaBr in benzonitrile, $AgNO_3$ in piperidine, $FeCl_3$ in pyridine and in benzaldehyde, and CoI_2 in $POCl_3$. In other cases the molecular conductivity at first increases and then decreases with dilution, *e.g.* $FeCl_3$ in paraldehyde, CBr_3COOH in $POCl_3$. Many solutions which, according to molecular weight determinations, are undissociated, conduct well. Thus $AgNO_3$ has a normal molecular weight in pyridine and benzonitrile, yet it conducts fairly well. According to Dutoit and Friderich, CdI_2, LiCl, NaI, $HgCl_2$ and NH_4CNS have normal molecular weights in acetone, and yet these solutions are conductors. Walden has found that KI, NaI, RbI, NH_4I and KCNS conduct well in liquid SO_2, and yet have abnormally large molecular weights in this solvent. Franklin and Kraus have found that while NH_4NO_3, $NaNO_3$ and KI dissolved in liquid ammonia are excellent conductors, the boiling points of the solutions are not nearly so high as they ought to be according to the ionisation theory. Nicolo Castoro found by means of the freezing-point method that $AgNO_3$, $CdCl_2$, $HgCl_2$ and $ZnCl_2$ have normal molecular weights in urethane; yet the author has found that the first three of these solutions are conductors. Recently, Innes found the molecular weights of succinic, salicylic and tartaric acids to be normal in pyridine according to the boiling-point method; preliminary tests by the author have shown that all three of these solutions are fairly good conductors.

In the case of non-aqueous solutions the various methods of observing ionisation do not always give the same indication with increasing dilution; it is sometimes in one direction and sometimes in the other. Occasionally simple substances in solution show abnormally low molecular weights, and yet are non-conductors. The author has found this to be so in the case of solutions of diphenylamine in methyl cyanide.

The abnormal behaviour, according to the theory, of non-aqueous solutions led the author to investigate aqueous solutions somewhat further.

Experimental Part.—The investigation consisted of four parts:—(1) Determination of boiling points of aqueous solutions of typical, common, chemical compounds from low to very high concentrations, to see how the molecular weight changes with the concentration. (2) Measurement of the conductivity of these solutions at or near their boiling points. These two parts of the work were carried out by Mr. A. A. Koch. (3) Measurement

[1] Abstract of a paper by Mr. Louis Kahlenberg in the *Journal of Physical Chemistry* (vol. v. pp. 339–392, June, 1901).

of conductivity at 0°. These determinations were made by Mr. R. D. Hall. (4) Cryoscopic determination of the molecular weights. The results of (1) and (2), and also of (3) and (4), were comparable, being under similar conditions.

The conductivity determinations were made by means of the usual Kohlrausch method with a telephone. The measurements at 0° were made in baths of melting ice. Those near the boiling point were not carried out at the boiling point, but at 95°, as small gas bubbles were apt to form at the electrodes at 100°. The freezing-point determinations were made with a regular Beckmann's apparatus of large size, about 40 grammes of water being used in each case. The solutions were cooled only from two to three tenths of a degree below their freezing points, and the crystallisation was inaugurated by means of a point of ice. The boiling-point determinations were made with a Beckmann's apparatus of about double the ordinary size, and thermometers graduated to 0°·01. It was at first thought best to surround the thermometer with a platinum cylinder in the boiling tube, as recommended by Jones, but fluctuations in the boiling point were found to result, apparently due to the solution within the cylinder being more concentrated than that without.

The water used was distilled in a block-tin condenser and had its conductivity reduced to 2×10^{-6} by drawing air through it free from carbon dioxide. In the results given, the conductivity of the water at the proper temperature has been deducted. Water of crystallisation was determined and allowed for in making up solutions, these being based on the amount of anhydrous salt present.

Conductivity measurements at 0° and at 95° are given for NaCl, KCl, KBr, KI, $MgCl_2$, $BaCl_2$, $HgCl_2$, $KClO_3$, KNO_3, $AgNO_3$, $MgSO_4$, $ZnSO_4$, $MnSO_4$, $CdSO_4$, $NiSO_4$, $CoSO_4$, $FeSO_4$ and $CuSO_4$. The volume in litres containing a gramme equivalent was varied from ¼ to 8192 in the case of the determinations at 0°, and from ½ to 2048 in the case of those at 95°. The results show an increase of the equivalent conductivity with dilution and the same trend in the curves at the two temperatures, but they are not parallel. For example, the curve between equivalent conductivity and the cube root of the volume is nearly a straight line for $MgSO_4$ at 95°, but much more curved at 0°. Curves of salts belonging to any one group all have the same trend.

The freezing-point determinations include NaCl, $MgSO_4$, $ZnSO_4$, $MnSO_4$, $CdSO_4$, $NiSO_4$, $CoSO_4$, $FeSO_4$ and $CuSO_4$. The results are summarised below :—

Sodium Chloride.—For about 0·2 normal solution the molecular weight was found to be 32·6, equivalent to 79·4 per cent. ionisation ; for an approximately normal solution (the strongest used) the molecular weight was 31·7, equivalent to 84 per cent. ionisation. According to the conductivity tests the ionisation is about 79 per cent. for a 0·2 normal solution and 70 per cent. for the normal solution. The results are, therefore, about the same by both methods for the dilute solution, but whereas the ionisation increases rapidly with dilution according to the conductivity, it remains constant or diminishes according to the cryoscopic method. This result is confirmed by the work of C. Dieterici and of R. W. Wood.

Magnesium Sulphate.—The limits were about 0·1 and 1·5 normal. The degree of ionisation for the first was 40 per cent. and for the second only 5 per cent. According to the conductivity measurements the ionisation should be 44 and 22 per cent. respectively, showing an increasing discrepancy with concentration.

Zinc Sulphate shows no ionisation in a normal solution, yet the conductivity is nearly the same as that of $MgSO_4$, and indicates 24 per cent. ionisation. The molecular weight in the strong solutions was the normal.

Manganous Sulphate shows at first an increase of molecular weight with concentration and then a decrease. The same is true of $ZnSO_4$ and $CdSO_4$, and to a slight extent of $NiSO_4$, $CoSO_4$ and $CuSO_4$. According to the conductivity of these solutions, the ionisation increases constantly with the dilution, but according to the cryoscopic measurements there is first a decrease and then an increase with increasing concentration. An approximately N/4 solution of $MnSO_4$ gave a molecular weight of 125·2, or 21 per cent. ionisation, the conductivity method giving 35 per cent. In a solution giving a molecular weight of 146·5 the ionisation is 3 per cent., whereas conductivity indicates 20 per cent.

Cadmium Sulphate, though a good conductor, shows no ionisation except in the most dilute solution (3·071 gm. CdSO₄ in 100 gm. of water), which gave 12 per cent. ionisation, the conductivity indicating 30 per cent.

Nickel Sulphate appears to be un-ionised when the strength is 10 per cent., but the conductivity shows 22 per cent. ionisation. In the most dilute solution the two methods gave about the same result.

Cobalt Sulphate.—The freezing point shows no ionisation when the solution is 5 per cent. or stronger, whereas the conductivity indicates 26 per cent. when the observed molecular weight is 155·2. In the most dilute solution the molecular weight was 131·8, corresponding to 18 per cent. ionisation, the conductivity indicating 34 per cent.

Ferrous Sulphate also is un-ionised in 6 per cent. solutions or above, according to cryoscopic determinations, yet the conductivity indicates 24 per cent. ionisation when the observed molecular weight is 154·8 (*i.e.* above the normal), and ionisation should be absent. The most dilute solution showed a molecular weight of 135·8, or 12 per cent. ionisation, the conductivity indicating 30 per cent.

Copper Sulphate is like the last two salts. When the observed molecular weight is 163·9, corresponding to no ionisation, the conductivity indicates about 22 per cent. In the most dilute solutions tested the molecular weight corresponds to 38 per cent. ionisation and the conductivity to 32 per cent.

The results obtained with copper sulphate are as follows, similar results for the other salts being given in the original paper :—

Copper Sulphate ($CuSO_4$). Molecular Weight, 159·7.

Amount of CuSO₄ in 100 gm. water.	Lowering of freezing point.	Molecular Weight.
1·835	0·300	115·6
3·312	0·405	154·6
6·443	0·743	163·9
9·242	0·996	175·4
14·210	1·569	171·2

The agreement, therefore, of the methods, viz. conductivity and freezing points, is poor, even in the dilute solutions. Arrhenius originally gave figures from cryoscopic measurements indicating no ionisation for $MgSO_4$, $FeSO_4$, $CuSO_4$, $ZnSO_4$, $CdSO_4$ and CdI_2, whereas ionisation was indicated by conductivity. He sought to explain this, in the case of the sulphates, by polymerisation of the un-ionised molecules, basing this assumption on the fact that Hittorf found the migration numbers of $MgSO_4$ and $ZnSO_4$ to show a considerable variation with concentration. This was also true of CdI_2, for which Hittorf consequently assumed double molecules, and applied the same explanation to other salts of the magnesia series. This at first seems to justify the position taken up by Arrhenius. However, the latter has not applied the explanation to all salts of the magnesia series, but has assumed polymerisation simply for those salts that did not behave according to his theory. $MgCl_2$ is a case in point. Similarly, Hittorf found the migration numbers of $CaCl_2$, $BaCl_2$, $Ca(NO_3)_2$ and $Ba(NO_3)_2$ strongly dependent on concentration, but Arrhenius did not assume polymerisation, for these salts agree better with his theory. To assume polymerisation in the case of $MgCl_2$, $CaCl_2$ and $BaCl_2$ would render it difficult to explain the results of Jones and Chambers, who found a minimum for the molecular lowering between 0·1 and 0·2 normal, and that the lowering in concentrated solutions was as great as, or greater than, that corresponding to complete ionisation. These authors attempt to explain this by assuming that the salts form hydrates. Thus another theory is brought in to account for abnormally low freezing points, to explain which the ionisation theory was itself originally introduced. Results of a similar kind have been observed by C. Dieterici.

The boiling-point determinations given by the author refer to NaCl, KCl, KBr, KI, $MgCl_2$, $BaCl_2$, $HgCl_2$, $KClO_3$, KNO_3, $AgNO_3$, $MgSO_4$, $ZnSO_4$, $MnSO_4$, $CdSO_4$, $NiSO_4$, $CoSO_4$, $FeSO_4$ and $CuSO_4$.

In the case of NaCl, KCl, KBr and KI the molecular weights continually diminish with increase of concentration, finally becoming less than half the theoretical values, whereas the molecular conductivity increases regularly with the dilution.

The molecular weight of $MgCl_2$ and of $BaCl_2$ decreases with increasing concentration until it becomes less than one-third the theoretical value, but the conductivity in both cases increases with the dilution.

$HgCl_2$ shows no ionisation by the boiling-point method. The molecular weight increases with concentration. It might be assumed that polymerisation takes place and, further, that some of the molecules which are not yet polymerised are ionised and thus account for the conductivity, which, though low, increases with the dilution.

In the case of $KClO_3$, KNO_3 and $AgNO_3$ the molecular weight increases with concentration, and there is good agreement with the conductivity measurements. Thus $AgNO_3$ in the most dilute solution tested appeared to be ionised to the extent of 65 per cent., while the conductivity method showed 67 per cent. For a normal solution the boiling-point method indicated 54 per cent. and the conductivity 52 per cent. The agreement is closer at the boiling point than at the freezing point.

In the case of $MgSO_4$ the molecular weight begins, in the dilute solution (2·733 gm. in 100 gm. of water), with a value above the theoretical, indicating no ionisation; then it increases with the concentration, and finally decreases after passing through a maximum, the values in the concentrated solutions becoming less than the theoretical. But there is no irregularity in the conductivity values. What has been said of $MgSO_4$ applies also to $ZnSO_4$, $NiSO_4$ and $CuSO_4$. The same general behaviour is also exhibited by $MnSO_4$, $CdSO_4$, $CoSO_4$ and $FeSO_4$, except that the molecular weights of these salts, while first increasing and then decreasing with increase of concentration, always remain above the theoretical values. The molecular weight of the sulphates is less by the freezing-point results than by the boiling-point method. So that if it be assumed that the molecules are polymerised, this polymerisation is greater at the higher temperature.

A series of boiling-point determinations was made on a solution of cane sugar, as an example of a non-electrolyte. It was found that the molecular weight diminished appreciably as the concentration increased, becoming less than the normal (212 in a solution of 289·4 gm. in 100 gm. of water, as compared with the normal 342). But, as is well known, the solution does not conduct. A test with Fehling's solution showed that no invert sugar had been formed by the boiling. Solutions of H_3BO_3, on the other hand, show practically constant molecular weight with varying concentration.

Discussion of Results.—From the above results it appears that there are solutions which are excellent conductors and which, nevertheless, show a normal molecular weight of the solute. While in some cases the molecular weight increases with the concentration, thus agreeing qualitatively at least with the ionisation theory, in other cases the molecular weight decreases with increase of concentration, finally becoming less than what it ought to be even for complete ionisation. In other cases the molecular weight at first increases with concentration and then diminishes. But the conductivity of these solutions continually increases with dilution. There are cases, however, in which the conductivity at first increases with the dilution and then decreases, *e.g.* aqueous solutions of the alkaline hydroxides.

It follows, therefore, that there is no such connection between freezing points and boiling points of solutions on the one hand and their conductivity on the other as is claimed by the ionisation theory. Often there is not even a qualitative agreement. Want of agreement is to be found in the original table of Arrhenius, but this was ascribed to experimental errors.

Various properties of electrolytes have been explained by the ionisation theory. Thus the various additive properties of salt solutions are presented as supporting the theory. But the theory cannot be based on additive properties of this kind, for such are known to exist in the case of true chemical compounds, where, since there are no solutions under consideration and since there is no electric conductivity observable, the possibility of ionisation is out of the question. In the realm of physiology, also, the theory cannot cope with the facts.

The heats of neutralisation of acids and bases have been used as an argument in favour of ionisation; Crompton, however, has shown that the theory is not only unnecessary, but that it is inadequate. Again, the theory cannot be brought into harmony with the law of mass action, which is one of the strongest arguments against it.

The chemical reactiveness of electrolytes has been explained by attempting to ascribe to the ions a peculiarly strong chemical activity on account of the electrical charges that are supposed to reside upon them. In this connection attention is drawn to the action of water in frequently facilitating chemical action. While this fact may be in agreement with the ionisation theory, it cannot be used to support it; for there are many pure substances and mixtures that are very active, although there is no ground for assuming the presence of ions; *e.g.* many explosives. It is well recognised that many bodies unite with the solvent, and interaction then takes place between the new products, reactions taking place which might easily not occur between the original anhydrous bodies.

It has been supposed by Nernst and by J. J. Thomson that the higher the dielectric constant of a solvent the greater its ionising power. But many exceptions are now known, *e.g.* liquid NH_3, butyronitrile and pyridine (H. Schlundt), liquid SO_2 (Walden), liquid HCN, and amylamine.

That the ionising power of solvents is dependent upon the polymerisation of their molecules, as claimed by Dutoit and Aston, has been shown to be incorrect in many cases by Kahlenberg and Lincoln.

The ionisation theory is at its best in explaining electrolysis, but there are many phenomena which the theory does not explain. For example, why are the deposits of silver from some solutions poorly adherent and from others dense and well adhering, the potential difference and current density being the same?

As to the ionisation theory being required by thermodynamics, Clausius, who showed the discrepancy in the Grotthus theory, did not find it necessary to put forth such a radical hypothesis as that of Arrhenius. Nor did Hittorf find it necessary to frame such a theory. Finally, no marked improvements or discoveries in electrolysis are due to the theory. It has led to Nernst's theory of the E.M.F. of galvanic cells and a formula which really involves the assumption that the law of mass action is applicable to electrolytes in the sense required by the ionisation theory. That this law does not hold has already been mentioned. By maintaining the correctness of this formula and thus assuming that the law of mass action holds for electrolytes, Jahn has arrived at the conclusion (as clearly he must) that the ratio of the equivalent conductivity at a given concentration to that at infinite dilution does not correctly represent the degree of ionisation, and that the ionic velocities vary in dilute solutions. This has given rise to a discussion in the *Zeits. Phys. Chem.*

If the ionisation theory is not true, then the original difficulty with the van 't Hoff theory of solutions recurs, viz. the theoretical interpretation of the factor i in the gas equation. Of course this equation is supposed to hold strictly only for ideal gases. A normal solution, however, is rather dilute for many of the practical purposes of life. Not that one expects the gas equation to hold strictly for a normal solution, but what one has a right to expect from the modern theory of solutions is that, with increasing concentration, a solution should behave at least qualitatively as a gas does with increase of pressure. The ionisation theory does not satisfactorily explain the significance of the factor i. In any case this factor should never be placed equal to unity without experimental evidence, whether in connection with electrolytes or non-electrolytes.

Substances of similar chemical composition, when dissolved in the same solvents, behave similarly so far as boiling points or freezing points are concerned; this shows that the influence of the chemical nature of the solute affects these variations.

The analogy between gases and solutions has been pressed too far, so that it has been forgotten that we are dealing only with an analogy. The solution of a substance and the expansion of a gas are really very different. A gas will expand in vacuo or mix with any other gas, but a substance will not dissolve in every liquid. And here lies the difficulty of the theory. It neglects the all-important *rôle* of the solvent. It fails to emphasise the fact that the process of solution takes place because of a mutual attraction between solute and solvent, and this attraction is the essence of the so-called osmotic pressure, which is closely related to, if not essentially identical with, chemical affinity. The attraction between solvent and solute should be recognised. Each solution should be examined separately, beginning with the most concentrated, the behaviour of the most dilute solutions appearing as a limiting case; then we shall see the present theory of solutions in its true relation to the facts.

W. R. C.